



# Consecutive recovery of rare earth and alkaline earth elements by countercurrent electromigration in room temperature molten salts

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## Abstract

We have suggested the novel environmental harmonization process applying the countercurrent electromigration technique utilizing the room temperature molten salts substituted for the pyrometallurgical processes aiming at the recovery of the electrochemically base metals such as the rare earth and the alkaline-earth elements in spent catalysts. According to the batch experiments using ammonium imide type room temperature molten salts, the trivalent ions are drastically enriched at the anode and the results have lead to an efficient enrichment process under high-current density. Moreover, the development of the consecutive electromigration cell enables us to demonstrate that it is feasible to enrich the rare earth and the alkaline earth elements and to recover their salts in continuous parallel and multistage cleaning process.

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## 1. Introduction

Rare earth (RE) and alkaline earth (AE) metals and their compounds are characterized by a variety of physical properties permitting the versatile applications as functional materials. In recent, thermal resistant automotive three way catalysts were developed with remarkable notice to oxide materials including RE and AE metals such as supports and promoters. Such three way catalysts composed for the noble metal nano-particles on the insulating materials were containing the small amounts of RE and AE, which proceeded on the significant thermal stability and the catalytic activity. However, the practical recycle process for the spent catalysts was restricted for the precious noble metal and the recovery of the residual RE and AE in the spent catalysts has not reached the stage of practical use. Then, the importance of the recycle pro-

cess for the spent catalysis has been increasingly recognized so far. Therefore it is necessary to develop the recovery process for RE and AE metals considering from the economic and the environmental reasons for near future. For this purpose, we have applied the countercurrent electromigration for the development of the environmental friendly process [1] using the quaternary ammonium imide type room temperature molten salts (RTMS), which is recently focused on the hydrophobic, involatile and inflammable electrolytes [2–4]. In addition, this environmental harmonization process does not require a large number of steps compared with the conventional aqueous processes, because this new strategy of the environmental harmonization process has been extended from the conventional pyrometallurgical process [5–7]. In recent, a part of the significant results by the investigating the enrichment of RE and AE salts from the batch experiments has already been demonstrated. We have subsequently collected further data on the enrichment conditions and wish to report on the detail of our findings and present herein a

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detailed account of this methodology and its usefulness for the novel electromigration cell in order to recover the enriched salts from the solvent consecutively as technological application. The subject of this study was to widen the use of the electromigration process for the recycle of the spent catalysts.

## 2. Experimental

### 2.1. Preparation of room temperature molten salts

Two different types of the room temperature molten salts, a hydrophilic TMHA-TfO,  $[n\text{-C}_6\text{H}_{13}(\text{CH}_3)_3\text{N}][\text{CF}_3\text{SO}_3]$  and a hydrophobic TMHA-Tf<sub>2</sub>N,  $[n\text{-C}_6\text{H}_{13}(\text{CH}_3)_3\text{N}][\text{N}(\text{CF}_3\text{SO}_2)_2]$  were synthesized by the reaction of the trimethyl-*n*-hexylammonium bromide (Tokyo Kasei Kogyo),  $[n\text{-C}_6\text{H}_{13}(\text{CH}_3)_3\text{N}]\text{Br}$ , with the trifluoromethanesulfonic acid silver salt,  $\text{AgCF}_3\text{SO}_3$  (Wako Chem. Co. Ltd.) or with lithium bis((trifluoromethyl)sulfonyl)imide (Fluka),  $\text{Li}[\text{N}(\text{CF}_3\text{SO}_2)_2]$ . Each TMHABr and  $\text{LiTf}_2\text{N}$  was dissolved in the deionized water and TMHA-Tf<sub>2</sub>N salts in an organic phase were separated from the aqueous solution spontaneously. The dichloroethane was added into the mixture to extract the organic phase completely from the solution. The solvent cleaning procedure using 18 M $\Omega$  cm of the ultrapure water was performed at three times. The dichloroethane was evaporated and removed from the synthesized ionic liquids. Finally, the TMHA-Tf<sub>2</sub>N salt was dried in a vacuum chamber at 393 K for three days. The quality of the synthesized room temperature molten salts is ascertained from the fact that the yield of the product is 93%. It is also important to measure the amounts of water in the synthesized com-

pounds by the coulometric Karl Fischer Titration (DL32, Mettler-Toledo Ltd.) because some of them are hydroscopic. All the synthesized room temperature molten salts include the moisture less than 30 ppm.

### 2.2. Preparation of rare earth and alkaline earth salts

TfO salts of the RE and AE, e.g.,  $\text{LaTfO}_3$ ,  $\text{CeTfO}_3$ , and  $\text{BaTfO}_2$  (Tokyo Kasei Kogyo) were used as a reagent grade. The Tf<sub>2</sub>N salts of RE were synthesized from the bis((trifluoromethyl)sulfonyl)amine (Fluka) with lanthanum oxide or cerium carbonate (Wako Chem. Co. Ltd.). The residual rare earth oxide and carbonate were removed by the filtration. The solvent was evaporated and each white-colored RE salts were obtained. These RE salts were vacuum-dried in the chamber at 393 K for at least three days. The alkaline earth salts with Tf<sub>2</sub>N anion was synthesized from the similar procedures.

### 2.3. Consecutive countercurrent electromigration

The consecutive electromigration cell, we designed in order to recover the enriched salts continuously was depicted in Fig. 1. The U-shaped container for the RTMS bath was included a mixture of TMHA-TfO or TMHA-Tf<sub>2</sub>N equimolar composition with small amounts of rare earth and alkaline earth RTMS. The upper part of the both electrodes attached an outlet to eliminate the decomposition products. The electrode in the anode was employed for the graphite rod (3.0 mm inside diameter, Tokai Carbon Co., Ltd.) or the tungsten wire (1.0 mm inside diameter, Nilaco Co.). The lower part of the migration tube was

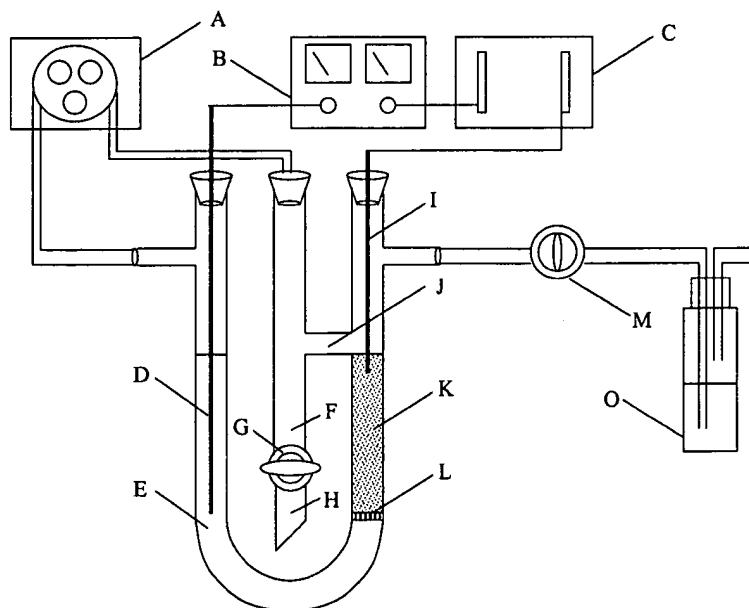


Fig. 1. The schematic diagram for the consecutive countercurrent electromigration using RTMS, A, roller pump; B, DC supplier; C, digital coulometer; D, tungsten wire (cathode); E, RTMS; F, recovering part of enriched RTMS; G, cock A; H, removing part of enriched RTMS; I, carbon rod (anode); J, sub-unit; K, alumina powder; L, glass filter; M, cock B; O, scrubber.

packed with the alumina powder, which has 75  $\mu\text{m}$  inside diameter (Wako Chemical Co. Ltd.) in order to prevent the convection of the melt in the migration tube. The bottom of the migration tube was attached with the glass wool. The bath temperature was kept at the intended temperature with a temperature controller (Shimaden Co. Ltd. DSL) and measured at a Chromel-Alumel thermocouple during electromigration. A constant DC current supplier (Anatec PowerPoreStar Model-3860) fed the constant electric currents. The total transported charge was measured by a digital coulometer (HIOKI 3187, AC/DC Power HI-TESTER). After more than several thousand coulomb of charge was transported, the enriched salts was sucked from the column and moved into sub-unit with use of the roller pump. The amounts of the enriched salts were regulated by the rotation rate of the pump. The amounts of quaternary ammonium ion ( $\text{TMHA}^+$ ) in each recovered salts were analyzed by the ion chromatography (Nippon DIONEX, ICS-1500). The amounts of rare earth and alkaline-earth ions were investigated from the inductively coupled plasma (ICP) emission spectrometry (Nippon Jarrell Ash, IRIS Advantage ICAP). All electromigration experiments were performed in a simply dry-box filled an argon atmosphere.

### 3. Results and discussion

The relative differences  $\varepsilon$  could be estimated from the chemical analysis and the transported charge quite similarly to the case of high-temperature molten salts. The  $\varepsilon$  values are calculated from the following equation based on the material and charge balances, which was derived from [8,9].

$$\varepsilon \equiv \frac{b_1 - b_2}{\bar{b}} = -\frac{F}{Q} \left( \frac{\sum n_1^i}{x_1} - \frac{\sum n_2^i}{x_2} \right),$$

where  $b_1$  is the internal mobility of the rare earth and alkaline earth cations 1, i.e., La, Ce and Ba,  $b_2$  the average internal mobility of the solvent, that is the TMHA-TfO or TMHA-Tf<sub>2</sub>N mixture of the equimolar composition,  $\bar{b}$  the average cation mobility of all the cations concerned,  $Q$  the transported charge,  $n_1^i$  and  $n_2^i$  the equivalents of cation 1 and cation 2 in the  $i$ th column of the separation tube from the anode to the position, where the chemical composition remained unchanged during electromigration, respectively, and  $x_M$  the mole fractions before electromigration.

#### 3.1. Enrichment of RE and AE in the RTMS

According to a series of the several runs in this study, the salt distribution along the tubes in each cell fraction in the TMHA-TfO including LaTfO<sub>3</sub>, CeTfO<sub>3</sub> and BaTfO<sub>2</sub> are presented in Fig. 2. The ordinate and the abscissa indicate the molar ratio of the target elements and the distance from the anode, respectively. The contents of La and Ce were drastically increased near the anode in comparison with those of Ba because the charge effect of the trivalent

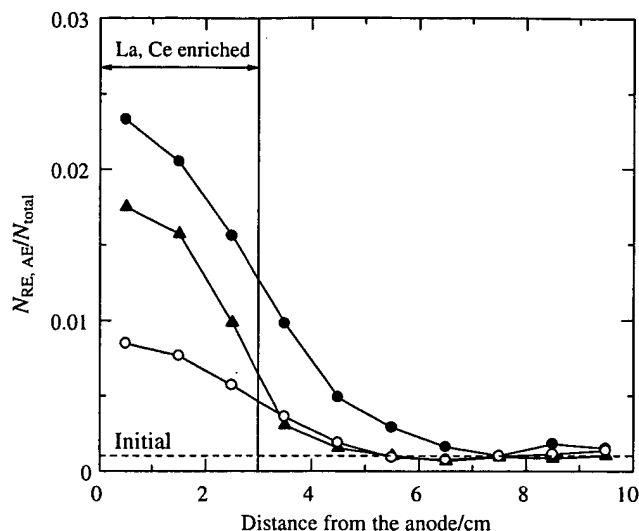


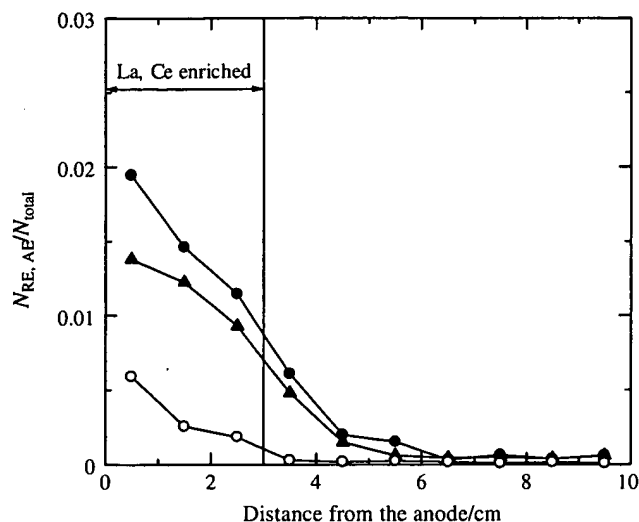
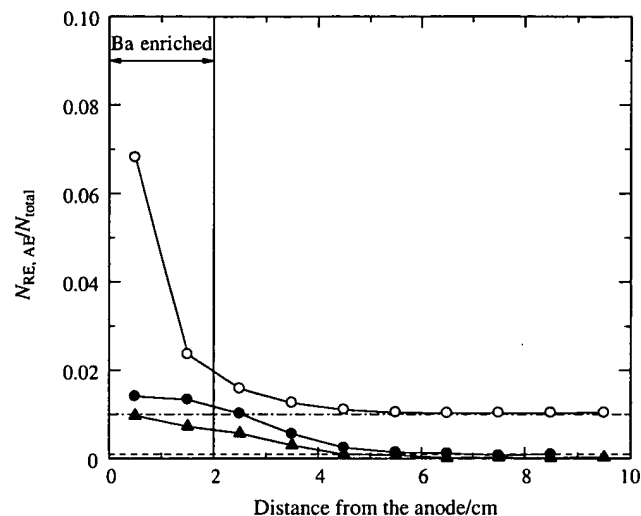
Fig. 2. The solute distribution profile in the migration tubes containing LaTfO<sub>3</sub>, CeTfO<sub>3</sub> and BaTfO<sub>2</sub> in TMHA-TfO at the similar concentration order. —●—:  $N_{\text{La}}/N_{\text{total}}$ , —▲—:  $N_{\text{Ce}}/N_{\text{total}}$ , —○—:  $N_{\text{Ba}}/N_{\text{total}}$ , the dotted line: initial composition.

ions influences larger than that of divalent ions in the electromigration process. The main experimental conditions and the relative differences were tabulated in Table 1. The negative values of  $\varepsilon$  implicates that the target elements migrate slower than the solvent components.  $-\varepsilon_{\text{La}}$  and  $-\varepsilon_{\text{Ce}}$  are apparently larger than  $-\varepsilon_{\text{Ba}}$ , which signifies that the trivalent cations migrate slower than the divalent cations. The molar ratios of La and Ce are larger than that of Ba in the first column because the elements with small ionic radius would be also affected on the enrichment of the target elements during electromigration. These experimental results were consistent with the reference concerned with the high-temperature molten salts [10]. Moreover, the enrichment of La, Ce and Ba with Tf<sub>2</sub>N salts was also confirmed from the batch experiments as displayed in Fig. 3. The electromigration process using the hydrophobic TMHA-Tf<sub>2</sub>N salts was applicable to the argon atmosphere at the relatively low temperature. The enrichment difference between TfO and Tf<sub>2</sub>N anions would be explained by the HSAB theory [11], which is recently reported that the trivalent lanthanide cations prefer TfO anion instead of Tf<sub>2</sub>N anion investigated by the spectroscopic and photochemical studies [12,13]. The trivalent lanthanide cation is a hard Lewis acid and it prefers to combine to the hard Lewis base, TfO anion, rather than to the soft Lewis base Tf<sub>2</sub>N anion. The fact that  $\varepsilon_{\text{La}}$  and  $\varepsilon_{\text{Ce}}$  values of TfO anion was relatively larger than those of Tf<sub>2</sub>N anion as tabulated in Table 2 would enable us to conjecture that the complex formation with TfO anion is more stable than that with Tf<sub>2</sub>N anion. Considering from the HSAB theory, because the Tf<sub>2</sub>N anions are weakly coordinated around the lanthanide cations, the lanthanum cation is relatively ease to be mobile and the mobility of the lanthanum cation would be large.

Table 1

The main experimental conditions and the relative differences for La, Ce and Ba with TfO anions at 373 K in the TMHA-TfO

No.	<i>x</i>	<i>Q/C</i>	<i>i<sub>d</sub></i> /A cm <sup>-1</sup>	$\epsilon_{\text{La}}$	$\epsilon_{\text{Ce}}$	$\epsilon_{\text{Ba}}$
1	0.01	1463	0.08	$-0.435 \pm 0.018$	$-0.415 \pm 0.016$	$-0.241 \pm 0.013$
2	0.01	1268	0.12	$-0.446 \pm 0.014$	$-0.396 \pm 0.012$	$-0.207 \pm 0.010$
3	0.01	1340	0.10	$-0.484 \pm 0.016$	$-0.432 \pm 0.014$	$-0.225 \pm 0.012$
4	0.01	1624	0.08	$-0.427 \pm 0.012$	$-0.374 \pm 0.013$	$-0.262 \pm 0.009$
5	0.01	1026	0.09	$-0.426 \pm 0.011$	$-0.381 \pm 0.012$	$-0.273 \pm 0.010$
6	0.01	1128	0.21	$-0.607 \pm 0.010$	$-0.568 \pm 0.011$	$-0.304 \pm 0.008$
7	0.01	1516	0.32	$-0.567 \pm 0.014$	$-0.542 \pm 0.016$	$-0.286 \pm 0.012$
8	0.01	1314	0.24	$-0.527 \pm 0.013$	$-0.505 \pm 0.014$	$-0.268 \pm 0.011$

Fig. 3. The solute distribution profile in the migration tubes containing LaTf<sub>2</sub>N<sub>3</sub>, CeTf<sub>2</sub>N<sub>3</sub> and BaTf<sub>2</sub>N<sub>2</sub> in TMHA-Tf<sub>2</sub>N at the similar concentration order. —●—:  $N_{\text{La}}/N_{\text{total}}$ , —▲—:  $N_{\text{Ce}}/N_{\text{total}}$ , —○—:  $N_{\text{Ba}}/N_{\text{total}}$ .Fig. 4. The solute distribution profile in the migration tubes containing LaTf<sub>2</sub>N<sub>3</sub>, CeTf<sub>2</sub>N<sub>3</sub> and BaTf<sub>2</sub>N<sub>2</sub> in TMHA-Tf<sub>2</sub>N at the condition that BaTf<sub>2</sub>N<sub>2</sub> contains one order more than LaTf<sub>2</sub>N<sub>3</sub> and CeTf<sub>2</sub>N<sub>3</sub>, —●—:  $N_{\text{La}}/N_{\text{total}}$ , —▲—:  $N_{\text{Ce}}/N_{\text{total}}$ , —○—:  $N_{\text{Ba}}/N_{\text{total}}$  the chain line: initial composition of Ba, the dotted line: initial composition of La and Ce.

It is possible to separate preferentially the higher enriched RE salts from the lower enriched AE salts under the condition of RE:AE = 1.0:1.0 as mentioned above. Supposing that the higher enriched rare earth elements were gradually removed from RTMS bath, the result of the salt distribution in the bath that AE contains ten time more than RE, that is, in the RE:AE = 0.1:1.0 is shown in Fig. 4. Although the first fraction contains the enriched RE, the AE salts was extremely concentrated in the first fraction. Furthermore, the influence of the current density concerned with the enrichment degree had been investigated in previous study [1]. The experimental results indi-

cated that the current density was strongly influenced on the enrichment degree of the first column in the concentration profile. We found it effective to enrich the trivalent ions under the condition at high-current density during electromigration. Our results are also consistent with the separation factor at the high-current density in the isotope separation of <sup>7</sup>Li/<sup>6</sup>Li [14]. Thus, the electromigration method can separate the trivalent cations from the divalent cations. In addition, the limiting current density under the electromigration is important factor to enrich

Table 2

The main experimental conditions and the relative differences for La, Ce and Ba with Tf<sub>2</sub>N anions at 323 K in the TMHA-Tf<sub>2</sub>N

No.	<i>x</i>	<i>Q/C</i>	<i>i<sub>d</sub></i> /A cm <sup>-1</sup>	$\epsilon_{\text{La}}$	$\epsilon_{\text{Ce}}$	$\epsilon_{\text{Ba}}$
1	0.01	1328	0.09	$-0.402 \pm 0.016$	$-0.395 \pm 0.014$	$-0.208 \pm 0.012$
2	0.01	1184	0.10	$-0.416 \pm 0.012$	$-0.382 \pm 0.011$	$-0.216 \pm 0.011$
3	0.01	1284	0.08	$-0.404 \pm 0.011$	$-0.363 \pm 0.010$	$-0.194 \pm 0.009$
4	0.01	1273	0.10	$-0.387 \pm 0.011$	$-0.344 \pm 0.012$	$-0.183 \pm 0.010$
5	0.01	1165	0.12	$-0.426 \pm 0.013$	$-0.367 \pm 0.012$	$-0.226 \pm 0.011$
6	0.01	1348	0.18	$-0.422 \pm 0.016$	$-0.398 \pm 0.014$	$-0.246 \pm 0.012$
7	0.01	1126	0.24	$-0.483 \pm 0.012$	$-0.423 \pm 0.012$	$-0.262 \pm 0.011$
8	0.01	1382	0.21	$-0.476 \pm 0.011$	$-0.416 \pm 0.010$	$-0.256 \pm 0.010$

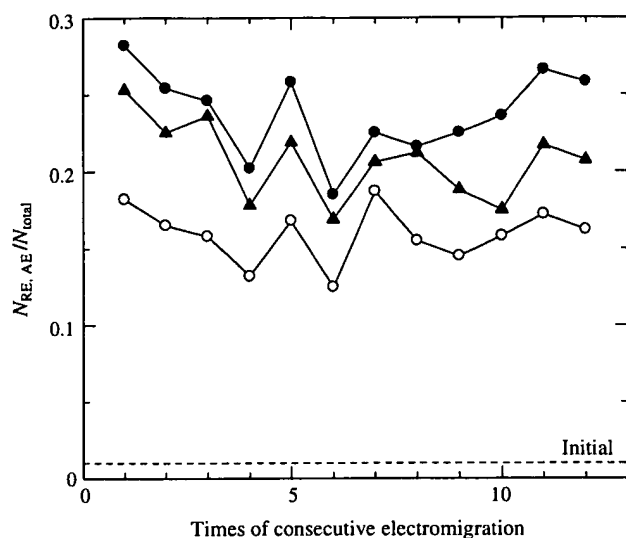


Fig. 5. The consecutive electromigration results No. 1; (La:Ce:Ba = 1.0:1.0:1.0) —●—:  $N_{La}/N_{total}$ , —▲—:  $N_{Ce}/N_{total}$ , —○—:  $N_{Ba}/N_{total}$ , the dotted line: initial composition.

the rare earth and the alkaline earth effectively because the current efficiency of the electromigration process is also influenced on the limiting current density. Therefore it is useful from steady-state voltammetry to estimate

the limiting current density for trivalent and divalent cations. Then the limiting current values for the recovery of these elements were needed to establish the electrodeposition process.

### 3.2. Consecutive countercurrent electromigration

It is important to recover the enriched RTMS after each electromigration process, because the enrichment parts were limited in the first fraction at the upper part of the anode. In addition, in the technological application of this practical electromigration process, it is essential to perform the successively operation. For this purpose, we have designed the novel electromigration cell as depicted in Fig. 1 in order to recover the enriched salts in the vicinity of the first fraction continuously and performed the electromigration process. The enriched salts were removed from the anode to the other recovering parts through the sub-unit under suction after each electromigration process. The suction of the enriched RTMS was executed using the roller pump under the condition of 15 rpm. A series of the experimental results were shown in Fig. 5 and the detailed experimental conditions were tabulated in Tables 3 and 4. The consecutive electromigration process was focused on the parallel and multi-stage removing process for RE and AE elements. The

Table 3

The main experimental conditions and the recovered salts after electromigration for La, Ce and Ba with  $Tf_2N$  anions in the RTMS

Run no.	$Q/C$	$i_d/A\ cm^{-2}$	Voltage/V	La/TMHA	Ce/TMHA	Ba/TMHA
Initial	—	—	—	$0.010 \pm 0.001$	$0.010 \pm 0.002$	$0.010 \pm 0.001$
a-1st	1264	0.16	50–65	$0.282 \pm 0.016$	$0.253 \pm 0.011$	$0.182 \pm 0.012$
a-2nd	1462	0.08	35–40	$0.254 \pm 0.014$	$0.225 \pm 0.012$	$0.165 \pm 0.010$
a-3rd	1228	0.14	35–45	$0.246 \pm 0.012$	$0.236 \pm 0.011$	$0.158 \pm 0.012$
a-4th	1326	0.16	40–55	$0.202 \pm 0.013$	$0.178 \pm 0.010$	$0.132 \pm 0.013$
a-5th	1434	0.12	35–50	$0.258 \pm 0.011$	$0.219 \pm 0.013$	$0.168 \pm 0.014$
a-6th	1126	0.09	35–40	$0.185 \pm 0.010$	$0.169 \pm 0.014$	$0.125 \pm 0.011$
a-7th	1338	0.12	40–50	$0.225 \pm 0.011$	$0.206 \pm 0.012$	$0.187 \pm 0.013$
a-8th	1416	0.10	35–40	$0.216 \pm 0.012$	$0.212 \pm 0.014$	$0.155 \pm 0.011$
a-9th	1428	0.16	40–50	$0.225 \pm 0.014$	$0.188 \pm 0.011$	$0.145 \pm 0.012$
a-10th	1142	0.18	45–55	$0.236 \pm 0.012$	$0.175 \pm 0.011$	$0.158 \pm 0.010$
a-11th	1216	0.24	50–65	$0.266 \pm 0.013$	$0.217 \pm 0.012$	$0.172 \pm 0.011$
a-12th	1108	0.21	55–70	$0.258 \pm 0.015$	$0.207 \pm 0.013$	$0.162 \pm 0.012$

Table 4

The main experimental conditions and the recovered salts after electromigration for La, Ce and Ba with  $Tf_2N$  anions in the RTMS

Run no.	$Q/C$	$i_d/A\ cm^{-2}$	Voltage/V	La/TMHA	Ce/TMHA	Ba/TMHA
Initial	—	—	—	$0.001 \pm 0.000$	$0.001 \pm 0.000$	$0.001 \pm 0.000$
a-1st	1642	0.20	55–70	$0.018 \pm 0.001$	$0.021 \pm 0.001$	$0.009 \pm 0.001$
a-2nd	1843	0.18	45–55	$0.018 \pm 0.003$	$0.016 \pm 0.001$	$0.010 \pm 0.002$
a-3rd	1342	0.12	35–45	$0.014 \pm 0.001$	$0.011 \pm 0.001$	$0.008 \pm 0.001$
a-4th	1482	0.24	60–75	$0.017 \pm 0.002$	$0.016 \pm 0.001$	$0.008 \pm 0.002$
a-5th	1545	0.18	50–65	$0.016 \pm 0.001$	$0.013 \pm 0.002$	$0.008 \pm 0.001$
a-6th	1624	0.20	55–70	$0.023 \pm 0.001$	$0.019 \pm 0.001$	$0.011 \pm 0.002$
a-7th	1782	0.12	40–50	$0.020 \pm 0.003$	$0.018 \pm 0.002$	$0.010 \pm 0.001$
a-8th	1648	0.16	45–55	$0.019 \pm 0.001$	$0.017 \pm 0.001$	$0.009 \pm 0.001$
a-9th	1520	0.18	50–65	$0.016 \pm 0.002$	$0.017 \pm 0.003$	$0.008 \pm 0.002$
a-10th	1564	0.14	50–60	$0.015 \pm 0.002$	$0.016 \pm 0.001$	$0.008 \pm 0.001$

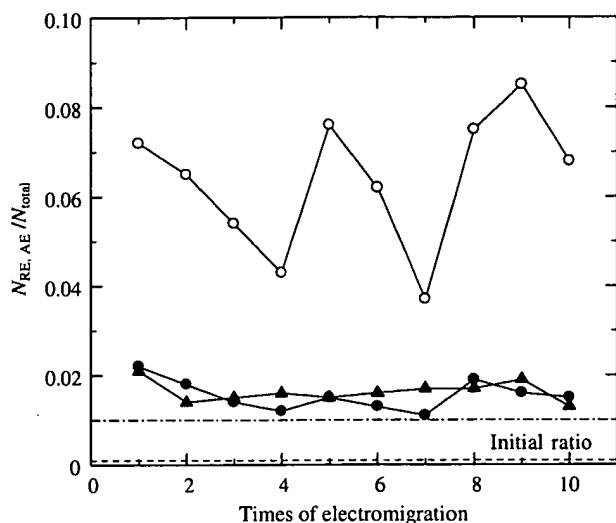


Fig. 6. The consecutive electromigration results No. 2; (La:Ce:Ba = 0.1:0.1:1.0) —●—:  $N_{La}/N_{total}$ , —▲—:  $N_{Ce}/N_{total}$ , —○—:  $N_{Ba}/N_{total}$  the chain line: initial composition of Ba, the dotted line: initial composition of La and Ce.

each recovered RE and AE ratios to the total components were much higher than the initial composition. This tendency was consistent with the batch experiments, that is to say, it is possible to separate preferentially the enriched RE salts from that of AE salts on the first separation process. It is also effective to recover the multivalent RTMS under the high-current density continuously in this stage. Moreover, after the enriched RE salts were removed, it is necessary to recover the residual lower enriched AE salts on the second separation process. The experimental results for consecutive electromigration at the condition of RE:AE = 0.1:1.0 were designate in Fig. 6. The enriched ratio of the recovered AE salts was about four to eight times larger than the bulk ratio, although RE salts were enriched in this stage. From the above all experimental results, these evidences enable us to conclude that the consecutive electromigration method using the RTMS was applicable to enrichment of multivalent cations and the salt bath multistage cleaning process. Finally, the consecutive electromigration process was successfully performed for twelve days without an obstacle and the multistage electromigration has lead to better enrichment and higher separation efficiency. For the future, we should estimate the energy required for the total electromigration process using the cumulative results as well as the fundamental data.

#### 4. Conclusion

We have performed a series of the electromigration experiments in the quaternary ammonium imide type room temperature molten salts in order to investigate the enrichment degree and the relative differences of the rare earth and the alkaline-earth elements. These experimental results revealed that it was effective to enrich the trivalent cations at high-current density and separate the trivalent cations from the divalent ones in RTMS. These separating motions concerned with the internal mobilities would be affected by the complex structures related with the charge and the ionic size of each cation. Moreover, we developed the originated consecutive electromigration cell and ascertained the functional smoothly work to enrich the rare earth and the alkaline earth elements continuously. Furthermore, this consecutive electromigration technique can contribute to not only the volume reduction of the RTMS bath wastes from the environmental friendly process but also the extension of the RTMS bath use.

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